PATENT SPECIFICATION

Convention Date (United States of America): Dec. 15, 1939. 545,838
Application Date (In United Kingdom): Dec. 13, 1940. No. 17647/40.
Complete Specification Accepted: June 16, 1942.

COMPLETE SPECIFICATION

Improvements in or relating to the Vulcanisation of Rubber

We, E.I. DU PONT DE NEMOURS AND CO., of Wilmington, Delaware, United States of America, a corporation organised and existing under the laws of the State of Delaware, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the vulcanisation of rubber and more particularly to accelerators for the vulcanisation of rubber.

The general use of 2-mercaptothiazoline as an accelerator of vulcanisation is known. The use of secondary accelerators to activate the cure, obtainable with a primary accelerator, is also known. It has generally been found, however, that it is impossible to use a secondary accelerator, such as an aldehyde-amine or a guanidine, with an acidic primary accelerator such as 2-mercaptobenzothiazole, because of the great activity of the combinations at processing temperatures. Secondary accelerators have been used successfully, however, with derivatives of 2-mercaptobenzothiazole, for example, a guanidine has been used with the benzyl ester of 2-mercaptobenzothiazole.

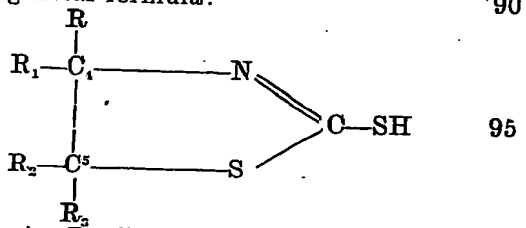
An object of this invention is to provide vulcanised rubber of improved properties, by employing as accelerators, in the vulcanisation process, a new combination of accelerators which are sufficiently safe at processing temperatures for commercial utilisation and which are at the same time very active at normal vulcanisation temperatures.

According to the present invention we incorporate in a rubber stock, prior to vulcanisation, a small proportion of a combination of primary and secondary accelerators, in which the primary accelerator is 2-mercaptothiazoline or a carbon substituted 2-mercaptothiazoline carrying as substituents one or more alkyl and/or hydroxyalkyl groups bonded to the ring carbon atoms of the thiazoline ring, and the secondary accelerator is an aldehyde-amine, arylguanidine and thiuram sulphide accelerator. We have found that such combinations of primary and secondary accelerators are sufficiently safe at ordinary processing temperatures to permit their use commercially, that is, such combination of accelerators does not tend to cause scorching or prevulcanisation to an objectionable extent so as to make their use impractical commercially. At the same time, such combination of accelerators show maximum activity at the usual vulcanising temperatures, and produce vulcanisates of high tensile strength and moduli.

We have found that the best results are obtained with 2-mercaptothiazoline itself as a primary accelerator. Of the carbon substituted 2-mercaptothiazolines, those in which the substituents are alkyl groups are generally preferred and we particularly prefer those in which the alkyl groups are lower alkyl groups, that is, contain from one to six carbon atoms.

By the term "alkyl" we mean aliphatic radicals consisting of carbon and hydrogen. By the term "hydroxyalkyl" we mean aliphatic radicals, which, except for the hydroxy group, consist of carbon and hydrogen. By the term "carbon substituted 2-mercaptothiazolines" we mean those in which the substituents are directly bonded to the ring carbon atoms of the thiazoline ring, that is, those in which the substituents are in the 4 of 5 or both the 4 and 5 positions.

The compounds employed as primary accelerators in the prevent invention have the general formula:



wherein R, R_1, R_2 and R_3 represent hydrogen or an alkyl or an hydroxyalkyl group.

While any of the aldehyde-amine, arylguanidine and thiuram sulphide accelerators may be employed, we preferably employ the aldehyde-amine

[Price 1/-]

accelerators, and particularly butyraldehydeaniline, known to the trade as "Accelerator 808". Of the arylguanidine accelerators, we prefer di-*o*-tolylguandine and diphenylguanidine. Of the thiuram sulphide accelerators, we preferably employ tetramethylthiuram monosulphide and tetramethylthiuram disulphide.

The combination of accelerators, employed in accordance with our invention, generally comprises from about 1 to 50 parts of the primary accelerator for each part of the secondary accelerator. When the secondary accelerator is an arylguanidine, it will generally be preferred to employ from about 1.5 to about 10 parts of the primary accelerator for each part of the arylguanidine. When an aldehyde-amine is employed as a secondary accelerator, it will generally be preferred to employ from about 2 to about 10 parts of the primary accelerator to each part of the aldehyde-amine. When a thiuram sulphide is employed as a secondary accelerator, it is preferred generally to employ from about 20 to about 50 parts of the primary accelerator to each part of the thiuram sulphide.

In order to show the safety of these combinations at the processing temperatures with the desirable properties obtainable at vulcanising temperatures, the following stocks were prepared. The base stock used in these tests is essentially the base stock of a modern inner tube.

Stock	A	B	C	D
Smoked sheets	100	100	100	100
Zinc oxide	5	5	5	5
Finely divided whiting	25	25	25	25
Stearic acid	1.5	1.5	1.5	1.5
Sulphur	2	2	2	2
2-Mercaptobenzothiazole	0.75	—	0.75	—
2-Mercaptothiazoline	—	0.75	—	0.75
Di-*o*-tolylguanidine	0.15	0.15	—	—
Butyraldehydeaniline	—	—	0.1	0.1

Stocks A and C, in which 2-mercaptobenzothiazole is used as the primary accelerator, were run for purposes of comparison with corresponding stocks B and D in which 2-mercaptothiazoline is used as the primary accelerator. The results of the vulcanisation tests on these stocks are given in Table I.

TABLE I.

Minutes Cured	Temp.	Stock A 500% Tensile		Stock B 500% Tensile		Stock C 500% Tensile		Stock D 500% Tensile	
60	227	1375	4300	350	1275	1425	4925	375	1550
45	287	1175	3500	1050	4000	1075	3775	1150	3475
60	287	1025	3025	975	3575	1025	3300	1000	3450

These results show (Stocks A and B) that, when di-*o*-tolylguanidine is used as the secondary accelerator, the stock (Stock B), in which 2-mercaptothiazoline is used as the primary accelerator, is very much safer than the one (Stock A), in which 2-mercaptobenzothiazole is used as the primary accelerator. It shows, in the 60 minutes cure at 227° F., a modulus at 500% of only 350 lbs./sq.in. compared with 1375 lbs./sq.in. for Stock A, while its tensile strength is only 1275 lbs./sq.in. compared with 4300 lbs./sq.in. for Stock A. On the other hand, in the cures at 287° F., the two stocks are substantially equal.

Essentially the same type of results are shown in the case where the butyraldehyde-aniline condensation product, sold under the trade name of "Accelerator 808", is used as the activating accelerator (Stocks C and D).

These tests show that it is possible to obtain vulcanisates having very desirable properties through the use of combinations of 2-mercaptothiazoline and secondary accelerators. Such vulcanisates may be processed with safety as is shown by the tests in which they were cured at 227° F. The extreme safety of these combinations permits a wide latitude in the selection of the accelerator combinations and the amounts of both the primary and secondary accelerators used in the

combinations.

In order to show that the results obtained above are not limited to the particular test formula used, the following stocks were prepared.

Stock	E	F	G
Smoked sheets	100	100	100
Zinc oxide	5	5	5
Channel black	25	25	25
Stearic acid	3	3	3
Sulphur	3	3	3
2-Mercaptothiazoline	0.9	0.97	0.9
Di-*o*-tolylguanidine	0.9	—	—
Tetramethylthiuram monosulphide	—	0.03	—
Butyraldehydeaniline	—	—	0.1

These stocks were cured for 30, 45, 60 and 90 minutes at 274° F. and the following test data were obtained.

TABLE II.

Minutes cured at 274° F.	Stock E 500% Tensile		Stock F 500% Tensile		Stock G 500% Tensile	
30	2300	4700	2450	5025	2375	4775
45	2700	5125	2875	4925	2775	5175
60	3075	4925	3000	4450	3025	4500
90	3275	4375	3275	4400	3275	4575

There was no difficulty in processing any of these stocks, but, as is shown in the table, when they were cured at 274° F., stocks having very high moduli and tensile strength were obtained.

When accelerating with a combination of accelerators, it is generally customary to use one, the primary accelerator, in much larger amounts than the other, the secondary accelerator or accelerator activator. Under these conditions, the properties of the vulcanisate more nearly approach the properties of a vulcanisate prepared from the primary accelerator alone than they do the properties of a vulcanisate prepared from the secondary accelerator alone. For example, vulanisates prepared from the guanidines alone are well-known to be very susceptible to rapid deterioration on ageing, i.e. they are poor "ageing" stocks. On the other hand, vulcanisates prepared from the thiazoles or thiazole derivatives are well-known to be extremely resistant to deterioration on ageing. When a small amount of a guanidine is used to activate the cure of a thiazole accelerator, the resulting vulcanisate has the age resisting characteristics of the primary thiazole accelerator. It has been found that vulcanisates, prepared by the combined use of a 2-mercaptothiazoline and a secondary accelerator, such as the guanidines, the aldehyde-amines and the thiuram accelerators, in which the thiazoline is used in a preponderant amount, likewise show characteristics which make them valuable commercial vulcanisates.

Stocks, obtained by this invention, have very good resistance to deterioration, particularly to deterioration on exposure to high temperatures. In order to show this effect, the following stocks were prepared. For purposes of comparison, tests were also made on an activated mercaptobenzothiazole derivative. For this comparison, the zinc salt of mercaptobenzothiazole was used instead of the free mercaptobenzothiazole, since it represents a combination of accelerators which can be handled commercially as contrasted with the activated free mercaptobenzothiazole which is very "scorchy".

Stock	H	I
Smoked sheets	100	100
Zinc oxide	5	5
Channel carbon black	50	50
Stearic acid	2	2
Pine tar	1.5	1.5
Phenyl-β-naphthylamine	0.6	0.6
"Thermoflex" A*	1.4	1.4
Sulphur	3	3
Zinc salt of 2-mercaptobenzothiazole	0.5	—
2-Mercaptothiazoline	—	0.5
"Accelerator 808"**	0.15	0.15

*"Thermoflex" A is the trade name of an antioxidant consisting of 50 parts phenyl-β-naphthylamine, 25 parts diphenyl-*p*-phenylenediamine and 75 parts of 4:4¹-dimethoxydiphenylamine.

**Accelerator 808" is the trade name of a butyraldehydeaniline condensation product.

Stocks H and I were cured for 60 minutes at 267° F. and showed the following tensile properties.

TABLE III.

Minutes cured at 267° F.	Stock H 500% Tensile		Stock I 500% Tensile	
60	2900	4375	3000	4675

These stocks were subjected to artificial ageing by suspending in an air oven at 100° C. for two days. After this time, Stock H had a tensile strength of 1925 lbs./sq.in. and an elongation at break of 420% while Stock I had a tensile strength of 2400 lbs./sq.in. and an elongation at break of 440%. Another type of ageing test was run by suspending these stocks in an oxygen bomb at 300 pounds oxygen pressure and at 70° C. After 14 days, Stock H had a tensile strength of 1375 lbs./sq.in. and an elongation at break of 420%, while Stock I had a tensile strength of 1800 lbs./sq.in. and an elongation at break of 460%. These tests show the extremely great resistance to deterioration exhibited by stocks cured with a combination of 2-mercaptothiazoline and a secondary accelerator.

Although certain definite combinations of activating accelerators with 2-mercaptothiazoline have been shown, those combinations are illustrative rather than limiting. It is also possible to use other guanidines, for example, diphenylguanidine or triphenylguanidine or the derivatives of the guanidines such as diphenylguanidine phthalate or tartrate or the zinc chloride addition products of the guanidines. Other aldehyde-amines, for example, butyraldehyde-butylamine, anhydro formaldehyde-*p*-toluidine, anhydro formaldehyde-aniline or methylene dianilide may be used. Other thiuram sulphide accelerators, for example, tetramethylthiuram disulphide may also be used in combination with 2-mercaptothiazoline.

Compounding ingredients and fillers, other than those shown in the test formulæ and in other proportions, may also be used.

While the tests have shown only the use of 2-mercaptothiazoline itself as the primary accelerator, equally good results can be obtained with the use of the carbon substituted 2-mercaptothiazolines in which one or both of the hydrogen atoms in the 4 or 5 or both the 4 and 5 positions of the thiazoline ring are substituted by alkyl groups or hydroxy-alkyl groups; such as, for example

4-Methyl-2-mercaptothiazoline
4-Ethyl-2-mercaptothiazoline
4-Propyl-2-mercaptothiazoline
4:4-Dimethyl-2-mercaptothiazoline
5:5-Dimethyl-2-mercaptothiazoline
4-Methyl-4-ethyl-2-mercaptothiazoline
4-Methyl-5-propyl-2-mercaptothiazoline
4:4-Dimethyl-5-propyl-2-mercaptothiazoline
4-Isopropyl-5-propyl-2-mercaptothiazoline
4:4-Dimethyl-5-propyl-2-mercaptothiazoline
4-Ethyl-5-propyl-2-mercaptothiazoline
4-Methyl-4-hydroxymethyl-2-mercaptothiazoline
4-Methyl-4-ethyl-5-propyl-2-mercaptothiazoline
4-Ethyl-5-methyl-2-mercaptothiazoline
4-Propyl-5-propyl-2-mercaptothiazoline

Having now particularly described and ascertained the nature of our said invention, and in what manner the same is to be performed, we declare that what we claim is:—

1. Process for the vulcanisation of rubber, characterised in that there is incorporated in the rubber mix, prior to vulcanisation, a small proportion of a combination of primary and secondary accelerators in which the primary accelerator is 2-mercaptothiazoline or a carbon substituted 2-mercaptothiazoline carrying as substituents one or more alkyl and/or hydroxy-alkyl groups, and the secondary accelerator is an aldehyde-amine, an arylguanidine or a thiuram sulphide, there being from about 1 to about 50 parts of the primary accelerator to each part of the secondary accelerator in the combination.

2. Process for the vulcanisation of rubber substantially as hereinbefore described.

3. Vulcanised rubber whenever produced by a process claimed in either of the preceding claims.

Dated the 12th day of December, 1940.
E. A. BINGEN,
Solicitor for the Applicants.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1942.